Covalent Crosslinking of Carbon Nanotube Materials for Improved Tensile Strength

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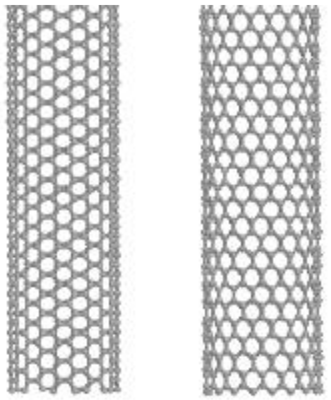
Carbon Nanotubes

SWCNT



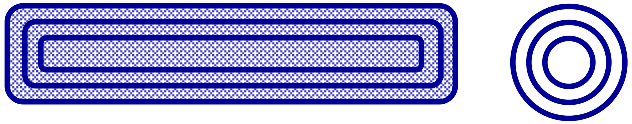
Source: Dai, H. *Acc. Chem. Res*, **2002**, *35*, 1035

Cylindrical structure of *sp*^{2} hybridized carbon atoms

Diameters- 1-50 nm
Lengths- 100nm- ~1 mm

Single-walled (SWCNT) or Multi-walled (MWCNT)

MWCNT

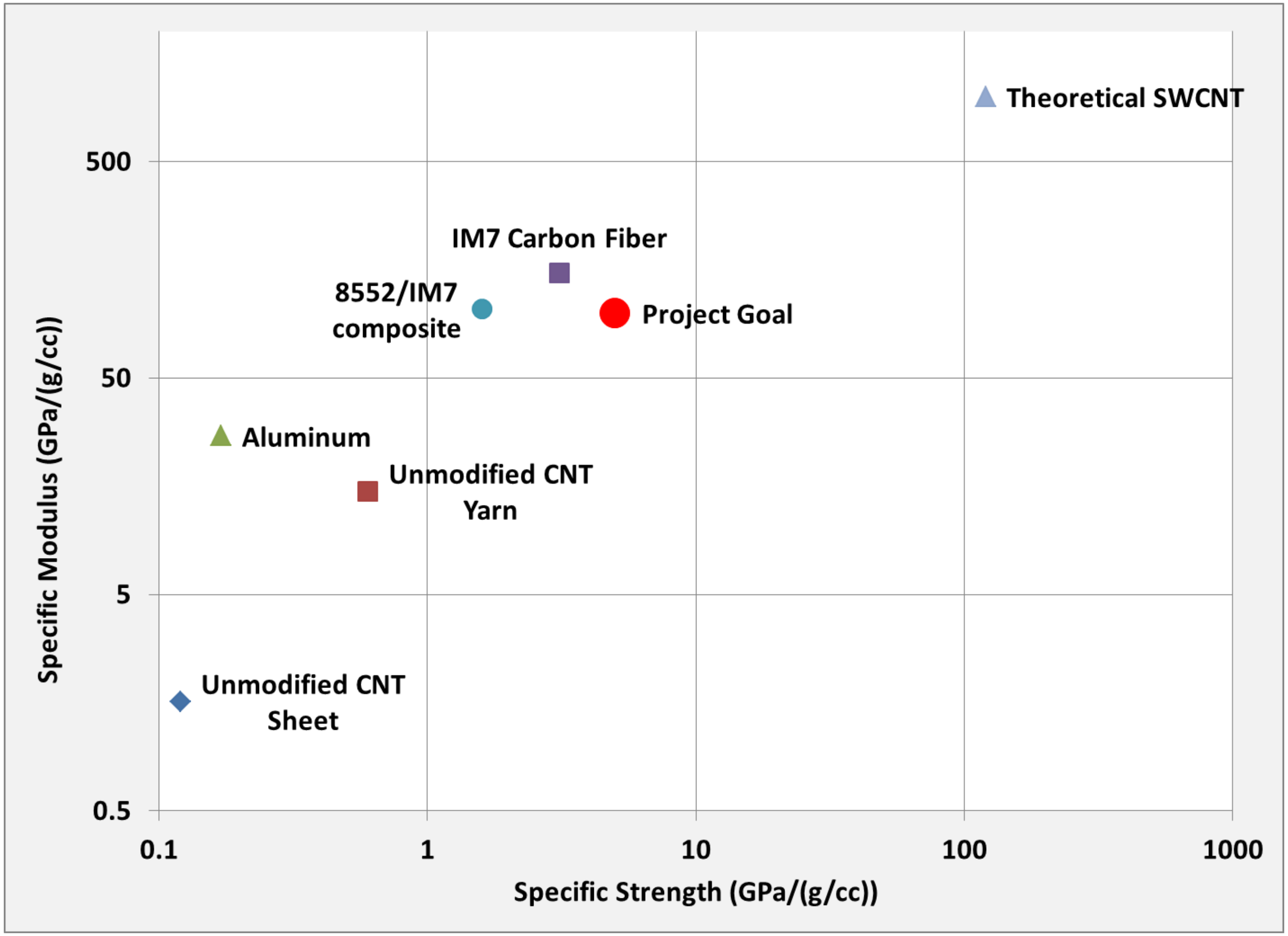


Properties:

- High strength and stiffness
- Low density (~1.6-2.2 g/cm^3)
- Good thermal and electrical conductivity
- High thermal stability

Naraghi, M.; Filleter, T.; Moravsky, A.; Locascio, M.; Loutfy, R.; Espinosa, H. *ACS Nano*, **2010**, *4*, 6463-6476
Lu, W.; Zu, M.; Byun, J-H.; Kim, B-S.; Chou, T-W. *Adv. Mater.*, **2012**, *24*, 1805-1833

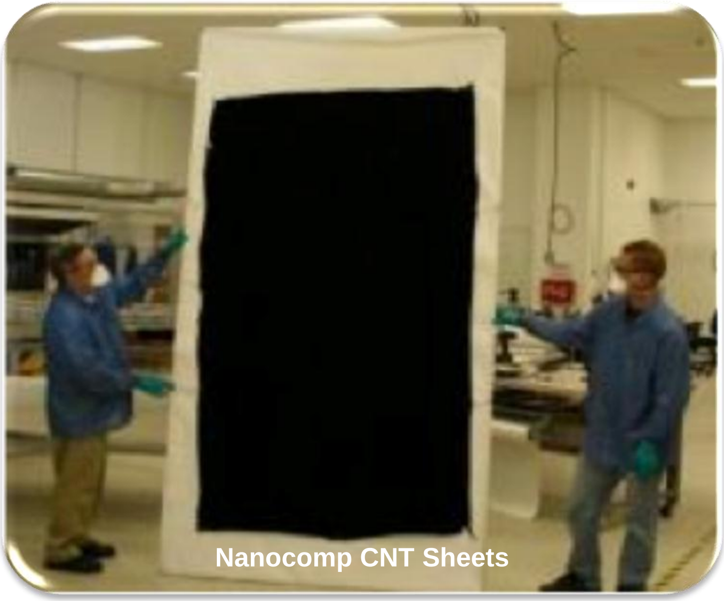
Project Goal

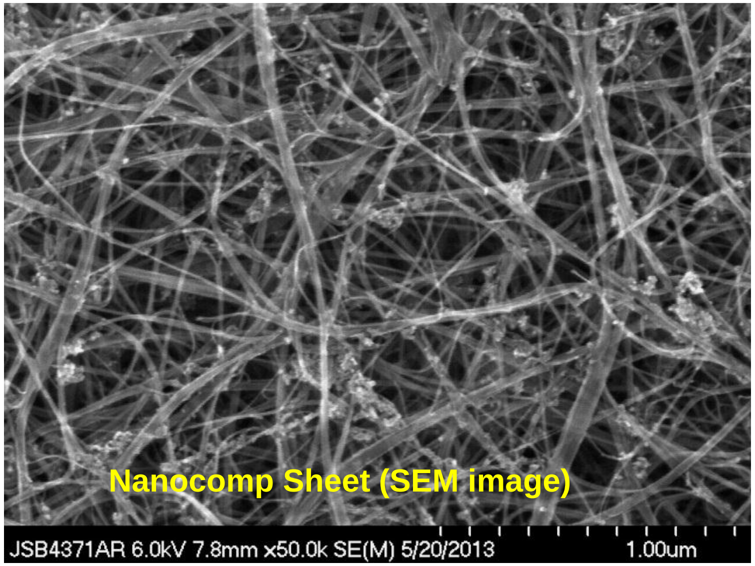


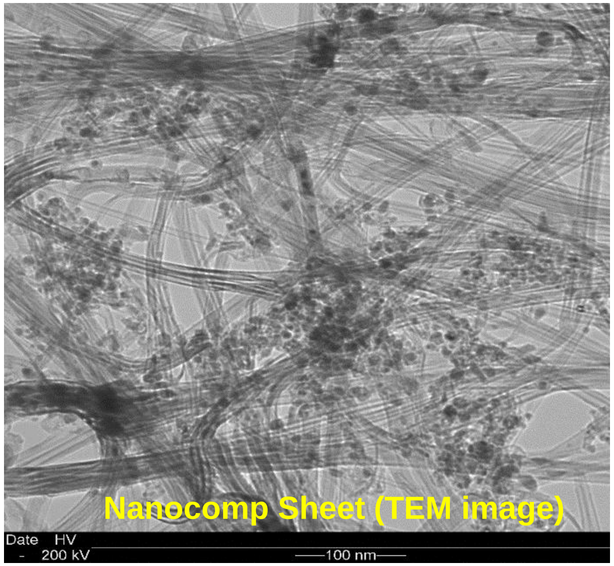
Improve strength to weight ratio of polymer matrix composite materials

- Reduce vehicle dry weight
  - ✓ Increase payload capacity
  - ✓ Lower fuel consumption

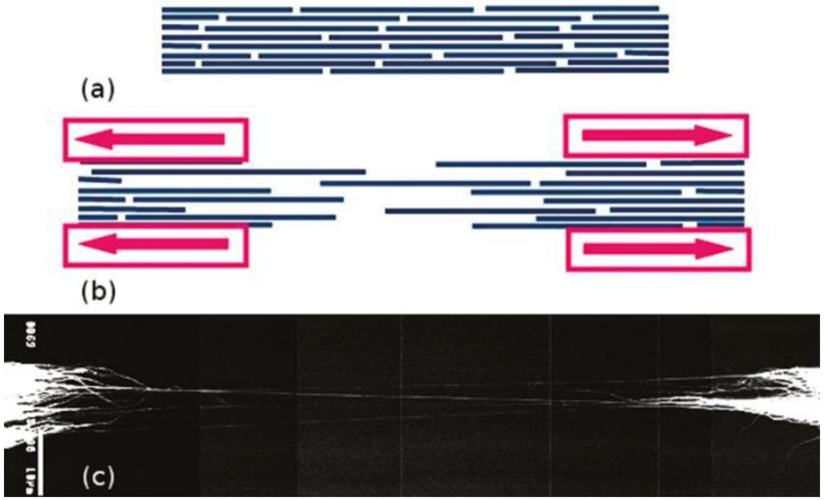
Carbon Nanotube Materials







Carbon Nanotube Yarns



Source: Vilatela,J.; Elliott, J.; Windle, A. *ACS Nano* **2011,** *3*, 1921-27

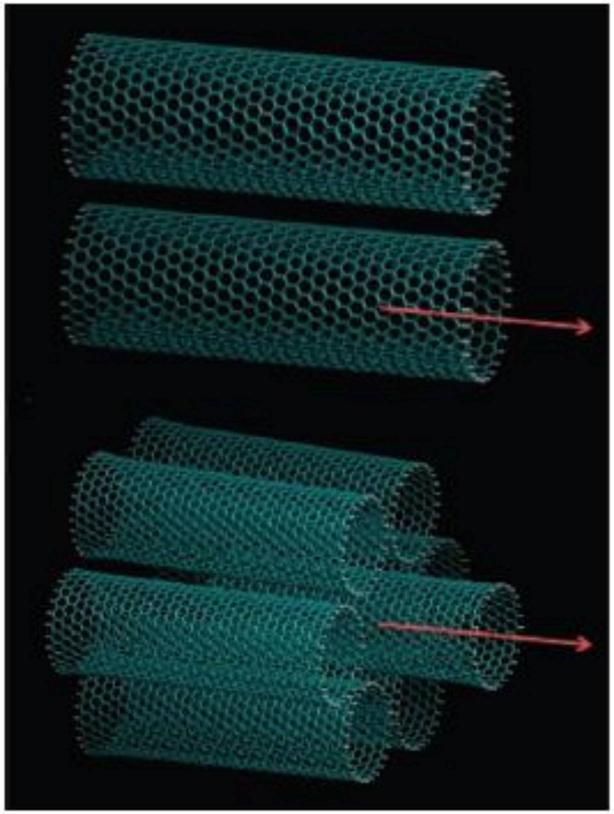
Carbon Nanotube tensile strength ~10-100 GPa

State-of-the-art carbon nanotube yarns ~3 GPa

Failure from slippage of nanotubes/bundles, not breakage of nanotubes

Windle, *et al*. (*Adv. Mater.,* **2010**, 4959; *ACS Nano*, **2011**, 9339)

Carbon Nanotubes



Source: Filleter, T.; *et al*. *Nano Lett.*, **2012**, *12,* 732

Nanotube tensile strength~ 10-100 GPa

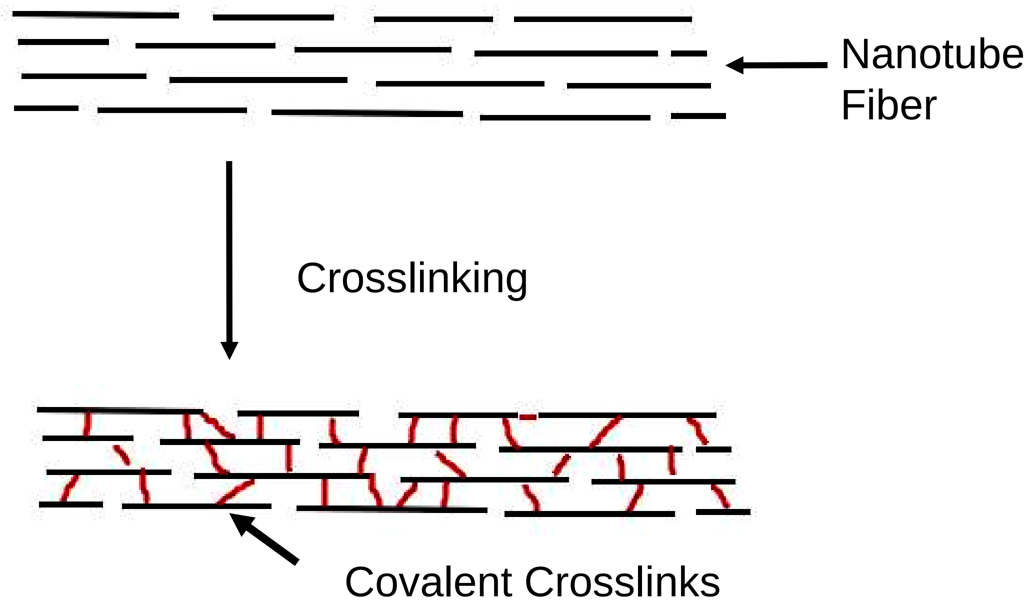
Inter-tube shear force= 0.5-10 MPa

Ease of sliding leads to poor load transfer between nanotubes

Need to increase inter-nanotube forces to take full advantage of nanotube tensile properties

Filleter, T.; Espinosa, H.D. *Carbon*, **2013**, *56*, 1-11

Our Proposed Solutions



Create covalent, inter-tube bonds to prevent tube-tube sliding.

- Chemical modification
- Electron beam irradiation

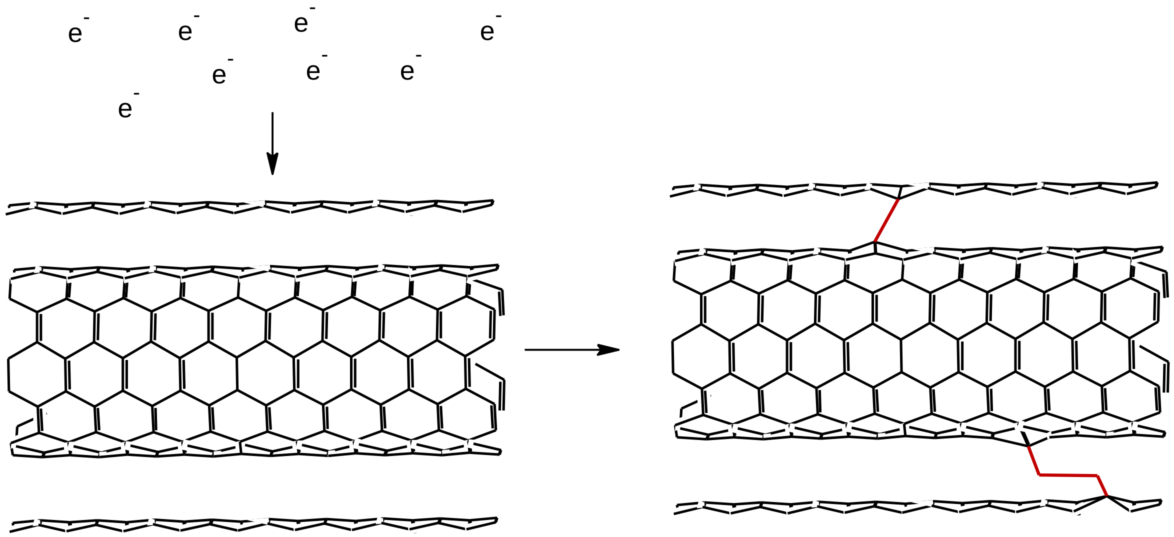
Increase inter-tube contact and alignment

- Solvent densification
- Stretching

Minimize damage to nanotubes during modification

Electron Beam Crosslinking

Irradiation of carbon nanotubes with high-energy particles can produce inter-shell or inter-nanotube covalent bonds

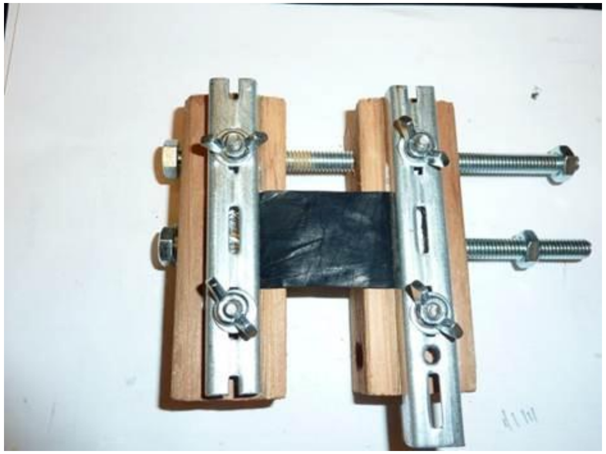


Filleter, T.; Espinosa, H. *Carbon*, **2013**, *56*, 1-11
Espinosa, H.; Filleter, T.; Naraghi, M. *Adv. Mater.*, **2012**, *24*, 2805-2823
Pregler, S.; Sinnott, S. *Phys. Rev. B,* **2006**, *73*, 224106

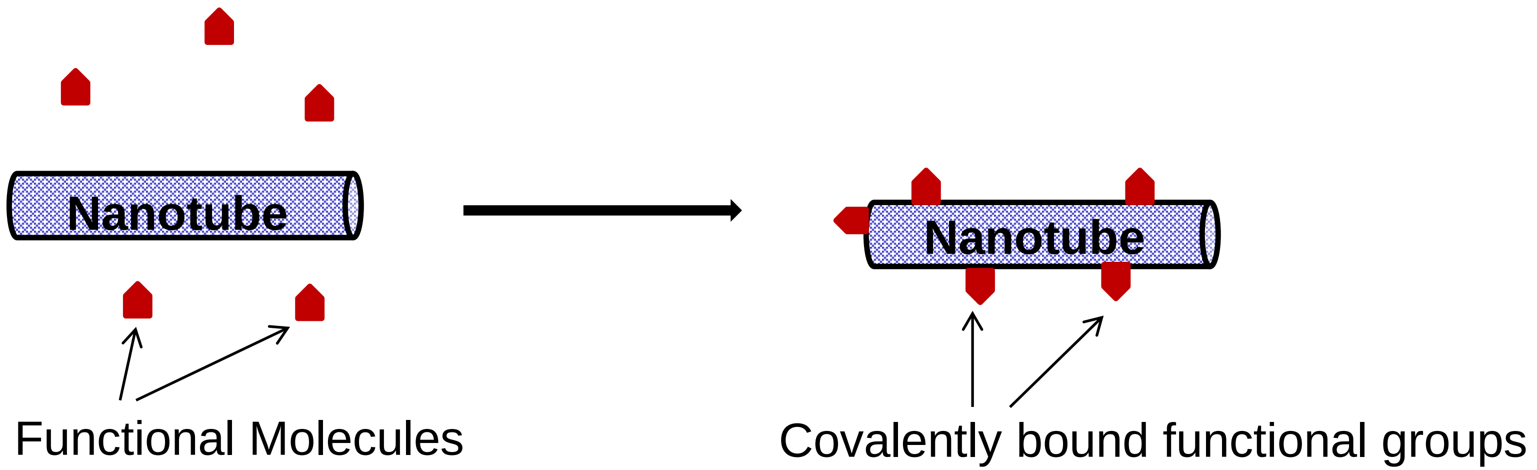
Prestraining

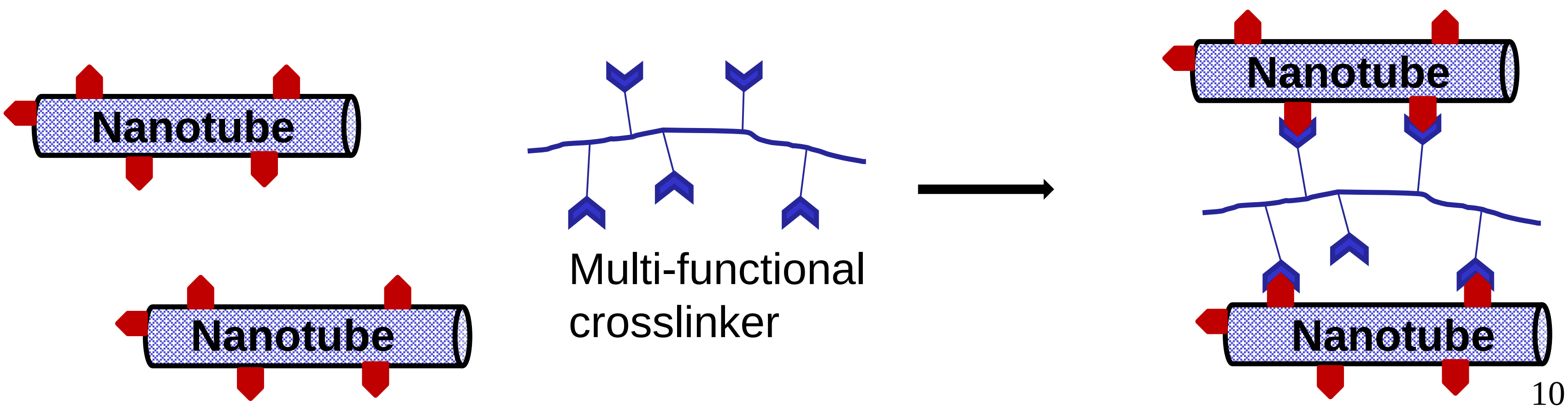
Drawing of yarns during spinning leads to improved nanotube packing and alignment

- Apply same principle to sheet material



Chemical Crosslinking



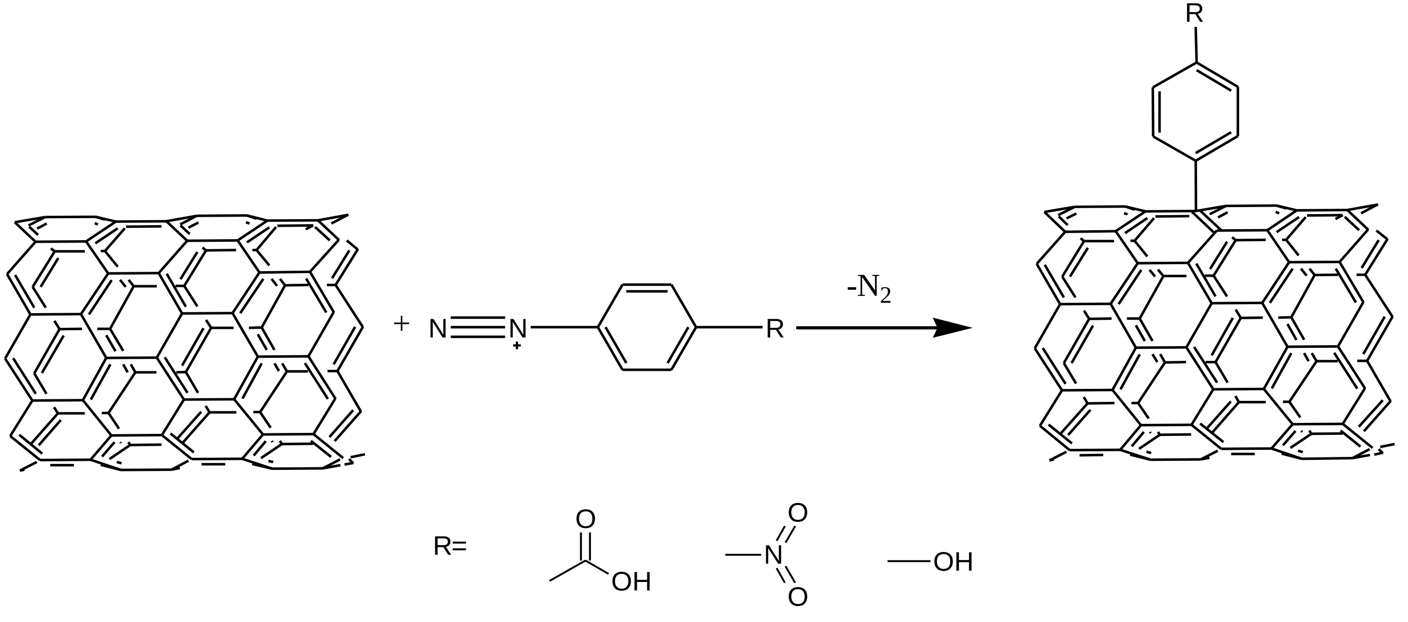


Aryl Diazonium

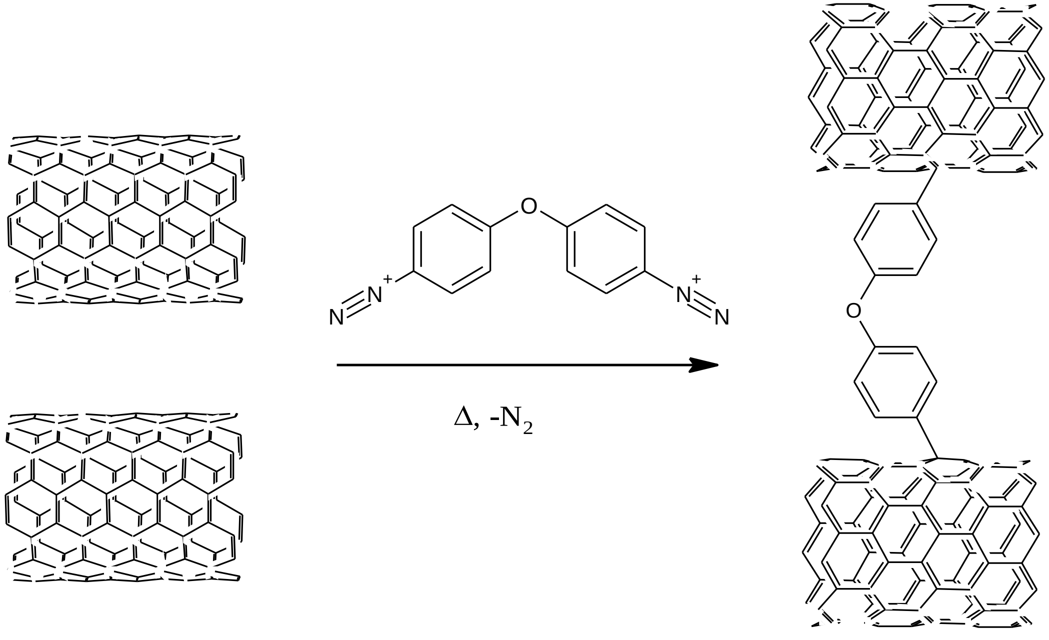
- Commonly used method for covalent functionalization of nanotubes (*Synlett*, **2004**, 155; *JACS*, **2003**, 1156; *Chem. Mater.*, **2001**, 3823)

- Use of *para*-functional anilines allows introduction of functional groups

- Using a di- or multi-amines should allow crosslinking of tubes

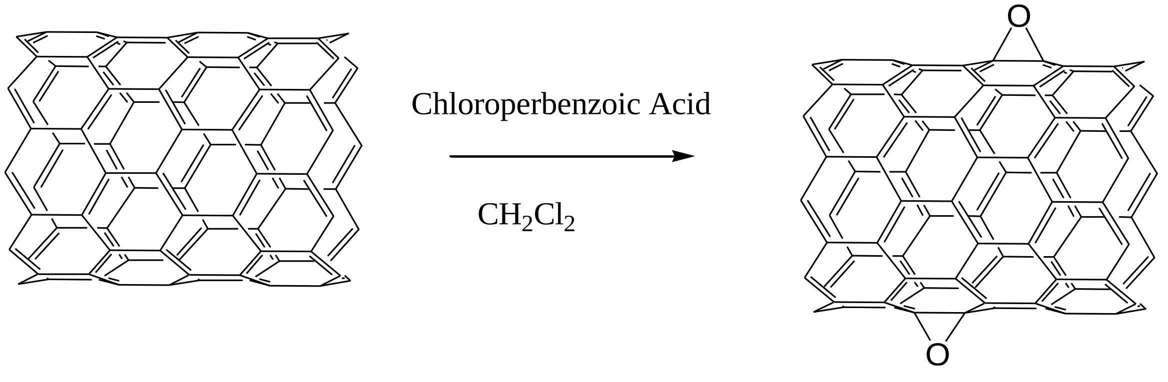


Aryl Diazonium

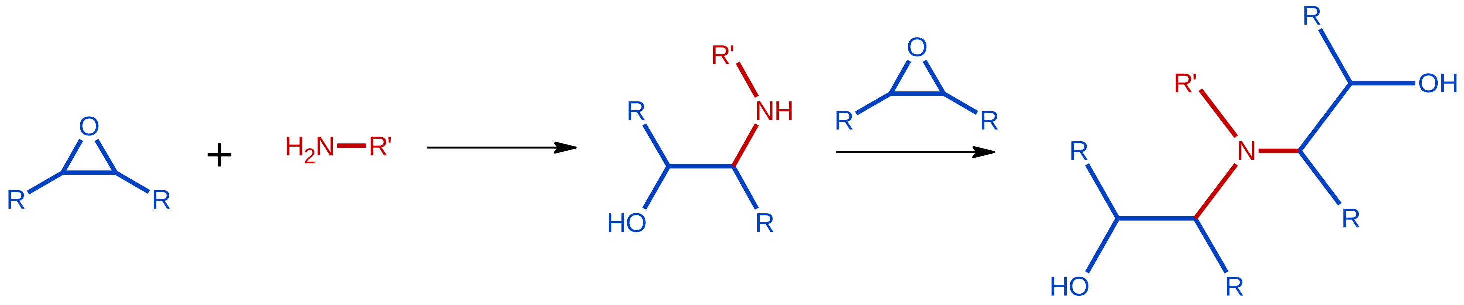


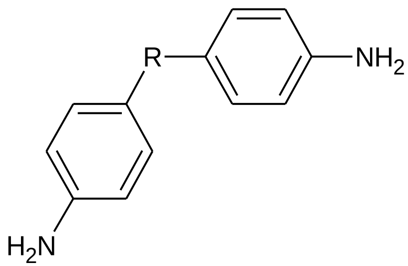
Epoxide Functional Nanotubes

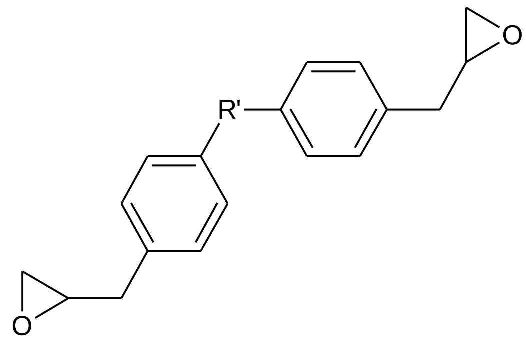
- Reaction with chloroperbenzoic acid (Prilezhaev reaction) can introduce epoxy rings on the nanotube surface (*JACS*, **2006**, 11322; *ACS Appl. Mater. Interfaces*, **2012**, 2065)

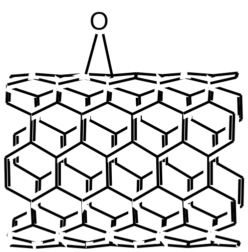


Epoxide Functional Nanotubes





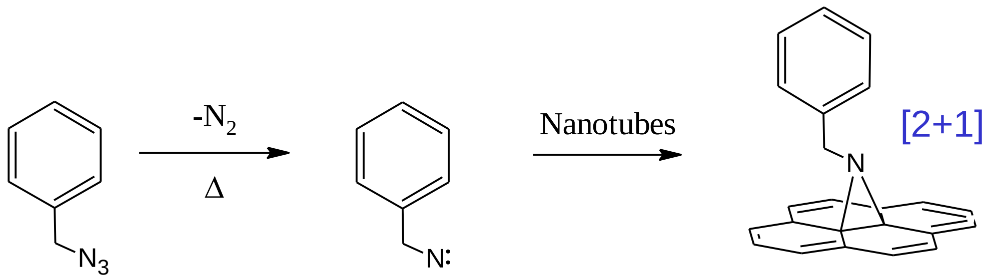




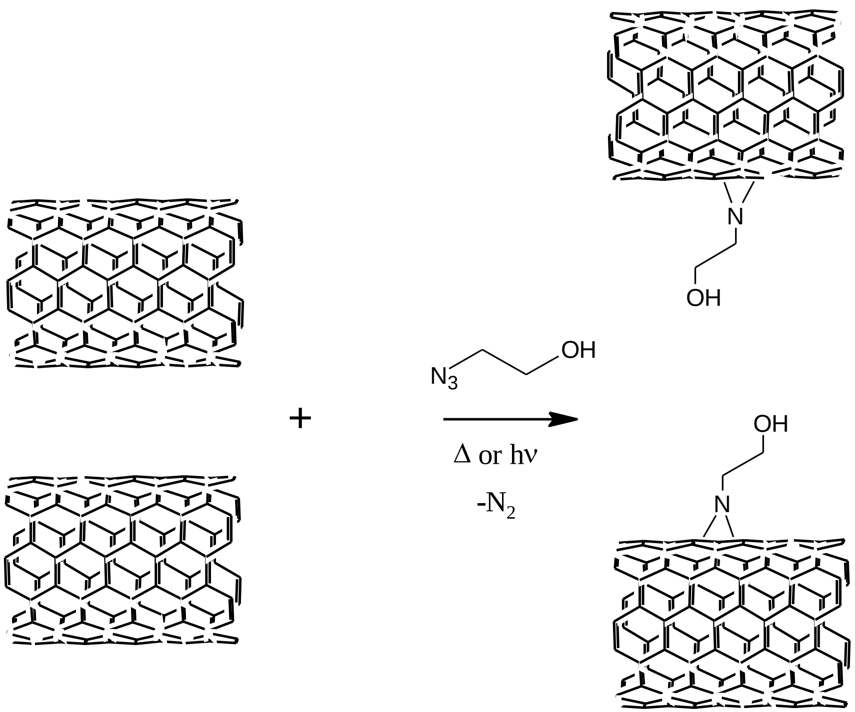
Epoxide rings on nanotubes can react with diamine during resin curing

- covalent attachment of nanotubes to resin matrix

Functionalization Using Nitrenes



[2+1] cycloaddition of nitrene to nanotube walls

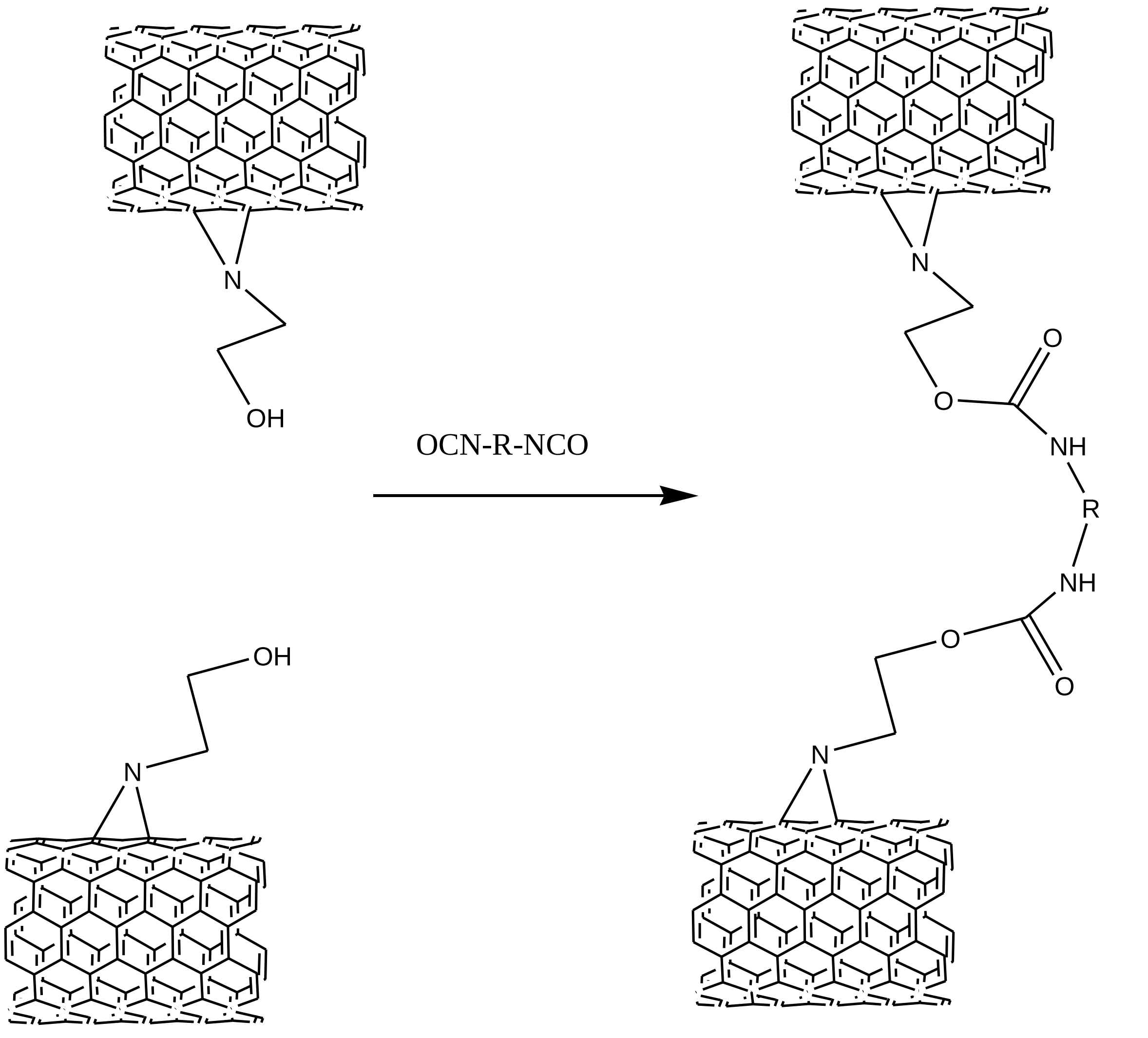


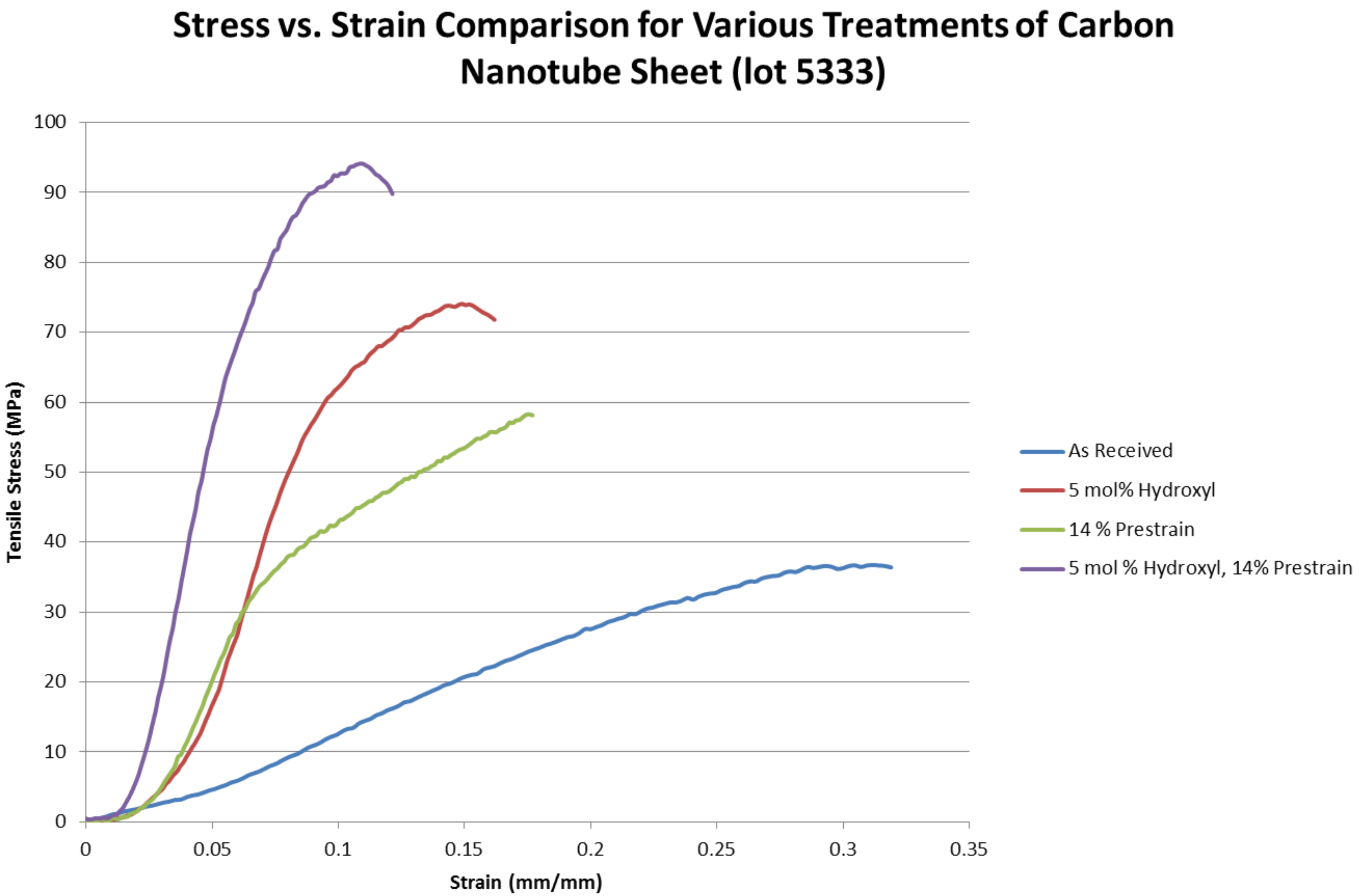
Hydroxyl Functional Nanotubes (CNT-OH)

Similar route for amine (CNT-NH$_2$)

Holzinger, M.; et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 4002; *JACS*, **2003**, *125,* 8566
Gao, C.; He, H.; Zhou, L.; Zheng, X.; Zhang, Y. *Chem. Mater.*, **2009**, *21*, 360

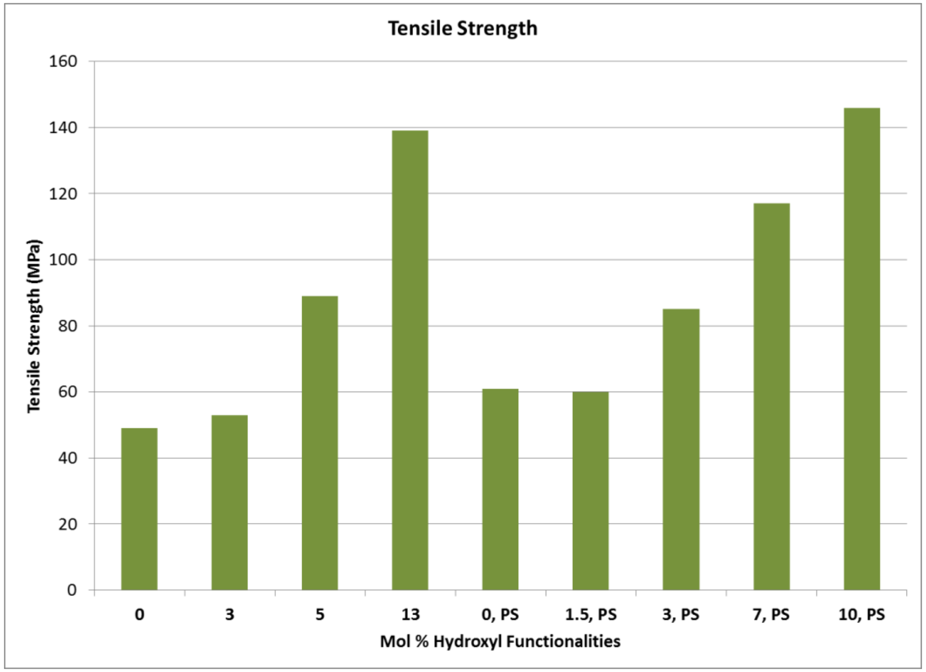
Nanotube Crosslinking Through Multifunctional Linkers

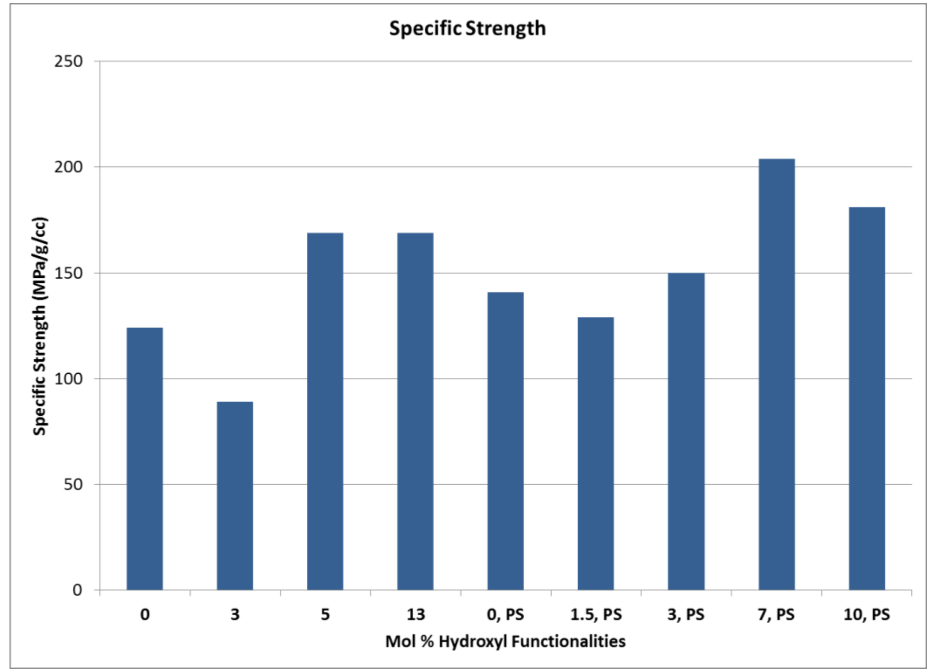




Functionalization results in:
- ✓ Higher tensile strength
- ✓ Higher tensile modulus
- ✓ Lower strain at break

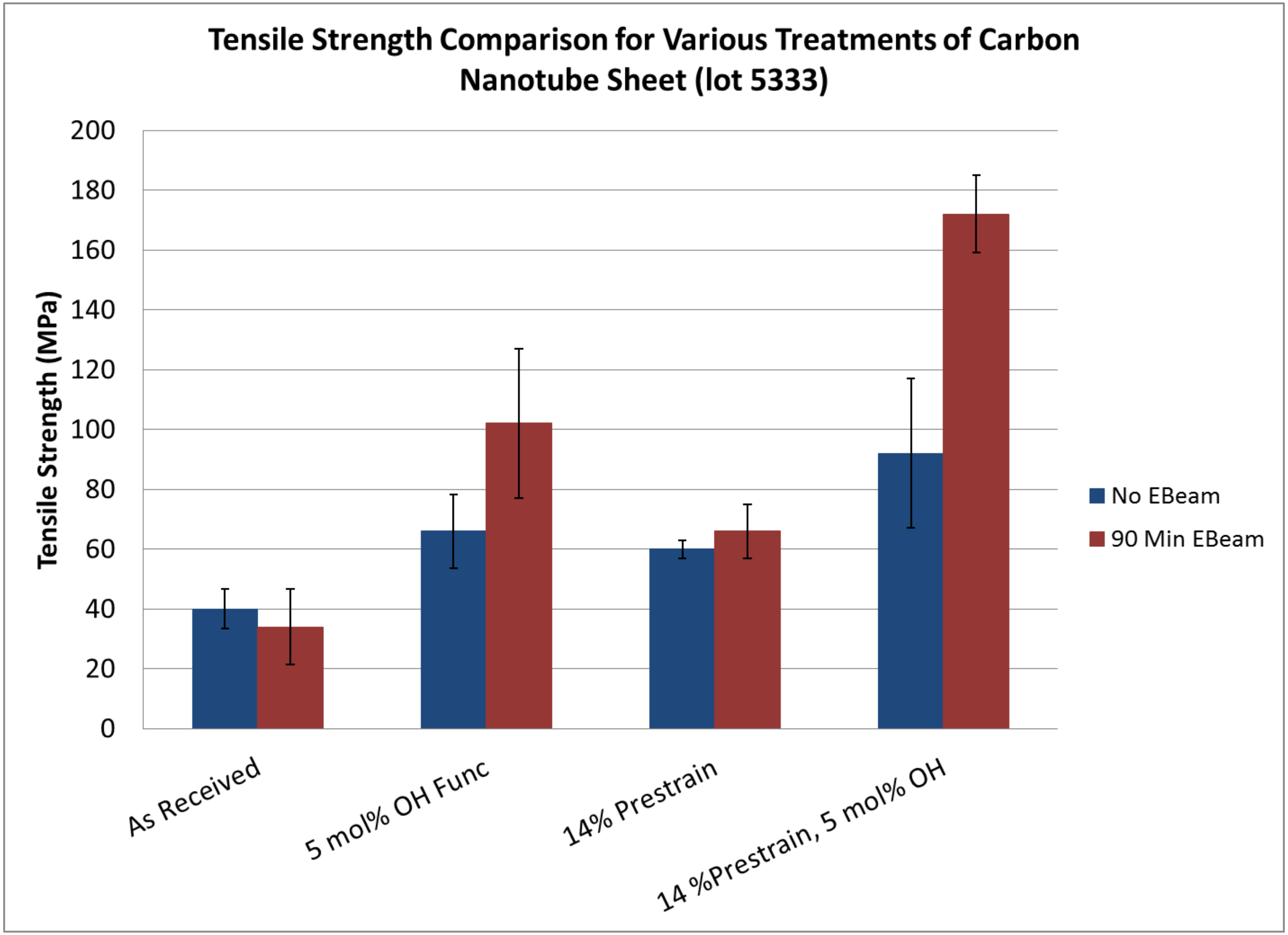
Effect of Degree of Functionalization



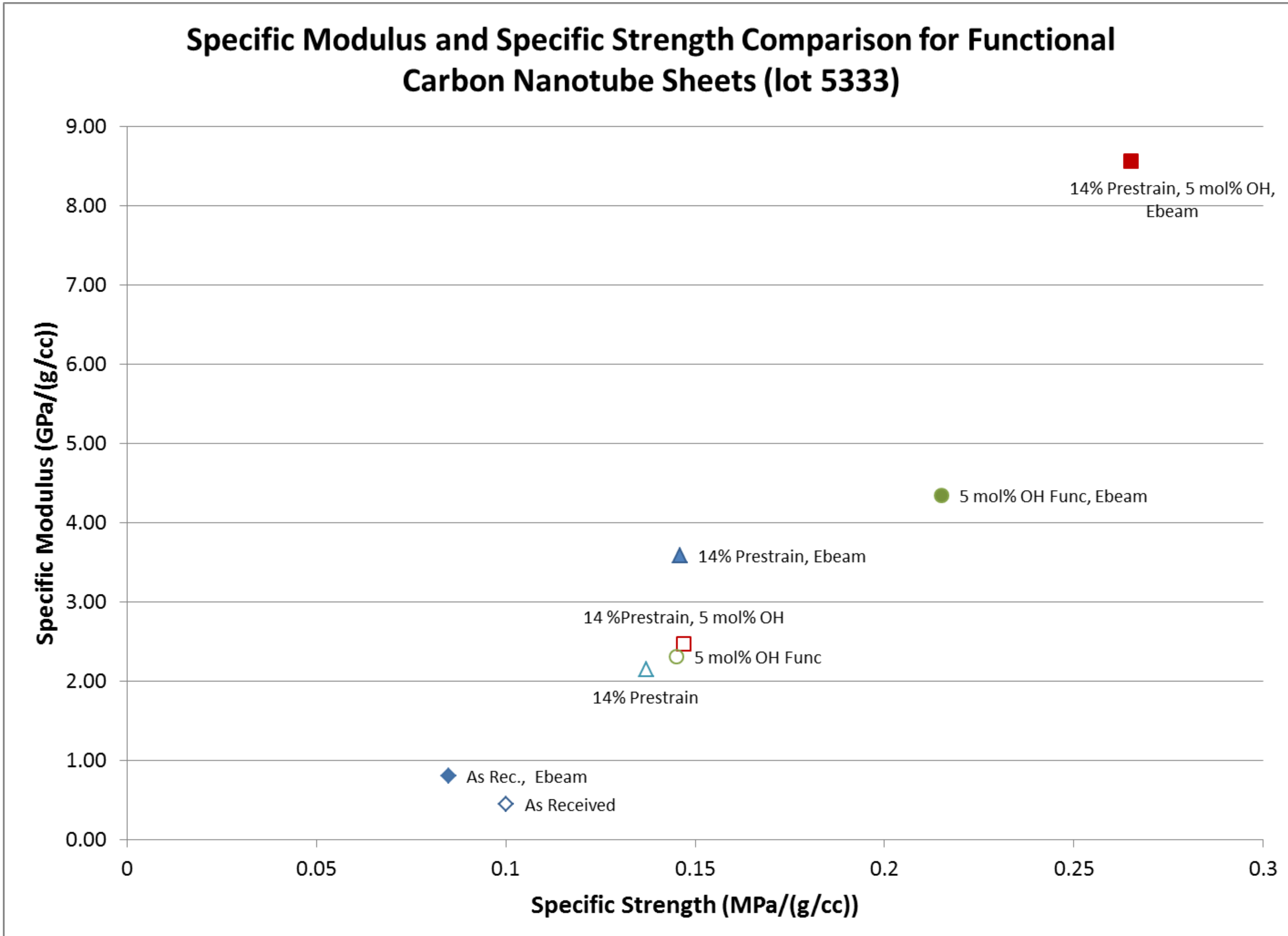


'PS' indicates 14% prestrained

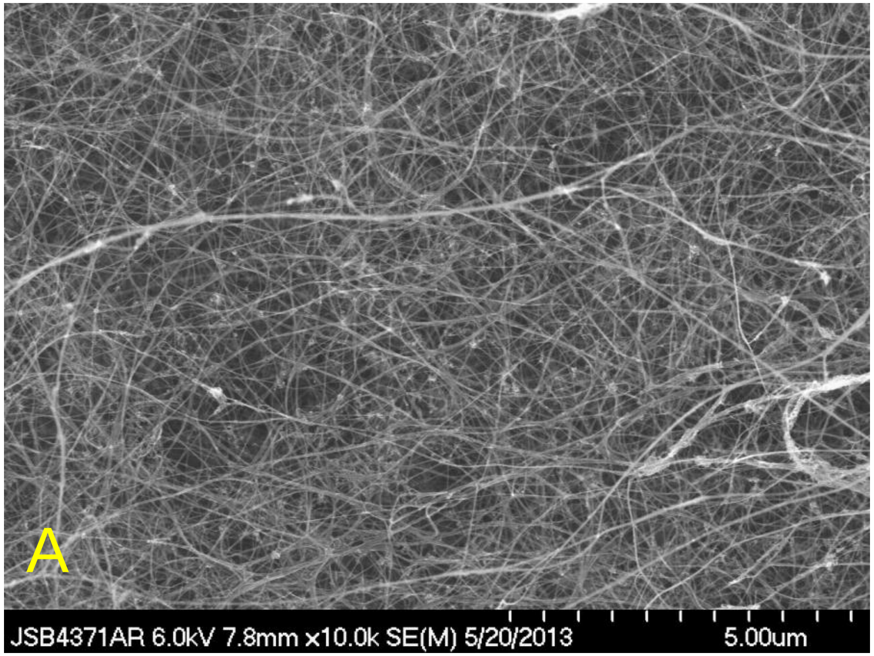
Optimal degree of functionalization is 5-10 mol% for best strength:weight ratio



Hydroxyl functional material prepared by reaction with azido ethanol (nitrene route)
E Beam irradiation, 90 min exposure, 2.2x 10^{17} e^{-} /cm^2 total fluence



Specific Modulus and Specific Strength Comparison for Functional Carbon Nanotube Sheets (lot 5333)
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Specific Modulus (GPa/(g/cc))
0
0.05
0.1
0.15
0.2
0.25
0.3
Specific Strength (MPa/(g/cc))
14% Prestrain, 5 mol% OH, Ebeam
5 mol% OH Func, Ebeam
14% Prestrain, Ebeam
14 %Prestrain, 5 mol% OH
5 mol% OH Func
14% Prestrain
As Rec., Ebeam
As Received

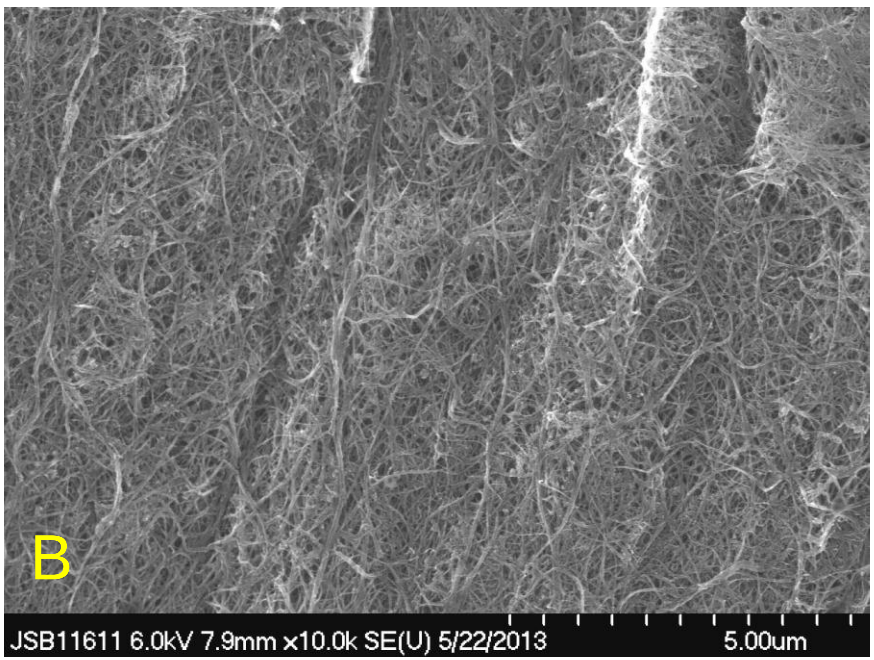


SEM Micrographs of Nanotube Sheet

A. As Received

B. 14% Prestrain, 5 mol% OH

C. 14% Prestrain, 5 mol% OH, 90 min E Beam



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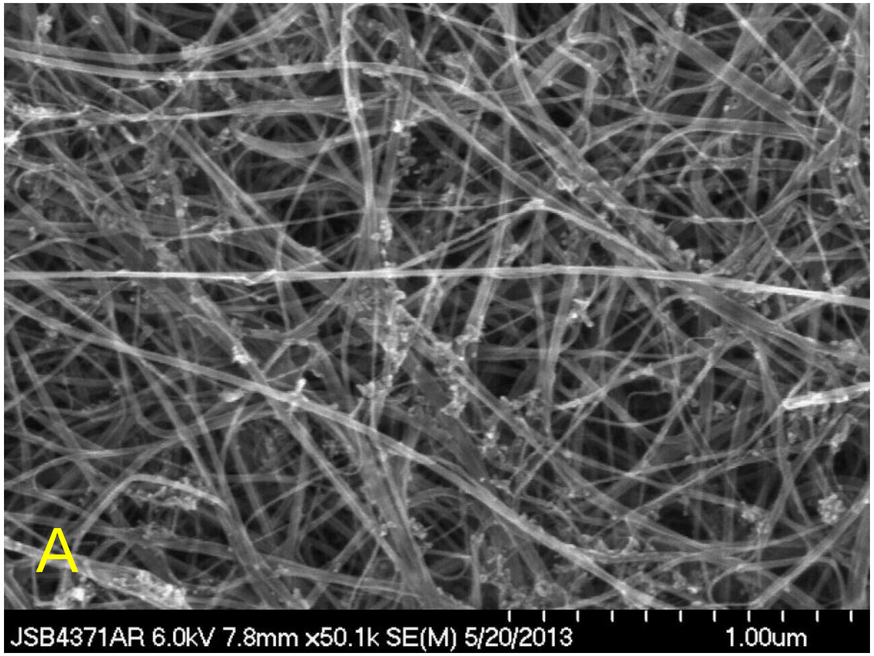

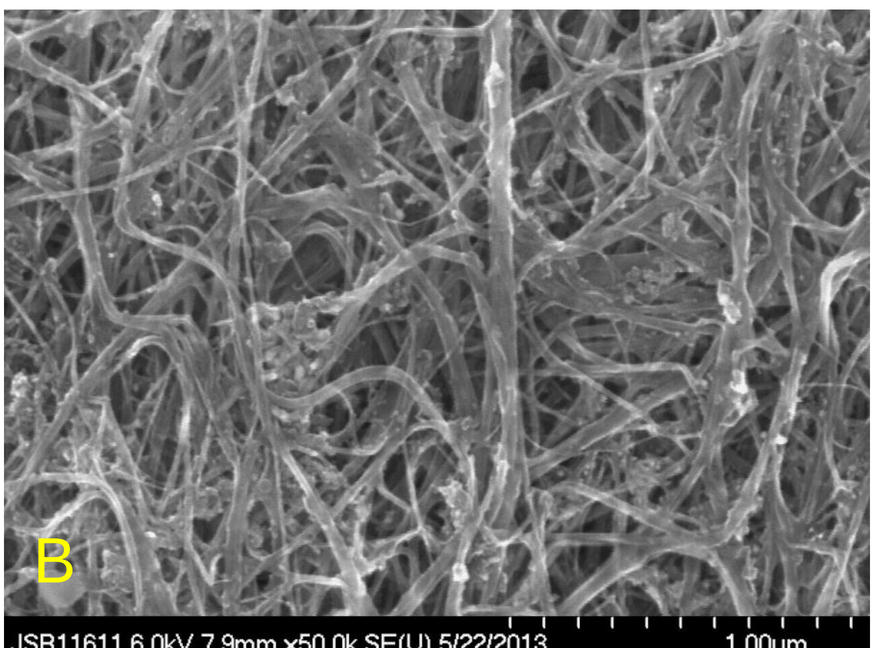

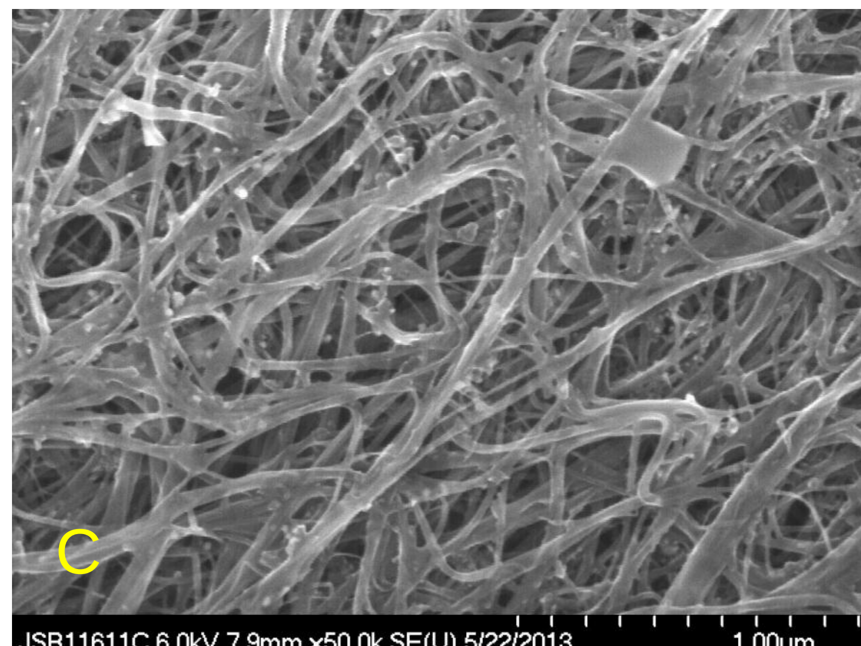

Summary

Several methods were examined that resulted in improved tensile properties for the carbon nanotube sheet material

- ✓ Covalent functionalization and crosslinking
- ✓ Electron beam irradiation
- ✓ Uniaxial prestraining

Generally, the methods evaluated resulted in an increase in material tensile strength and modulus and a decrease in strain at failure

Combination of these methods resulted in the largest improvement

> 14 % prestrain, 5 mol% OH, 90 min E Beam resulted in ~150% increase in specific strength and >10-fold increase in specific modulus over the as-received material

Currently evaluating performance of functional nanotube sheet material in polymer matrix composites

Acknowledgements

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- Dr. Tiffany Williams
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- Dr. Marisabel Lebron-Colon
- Dr. Jim Gaier

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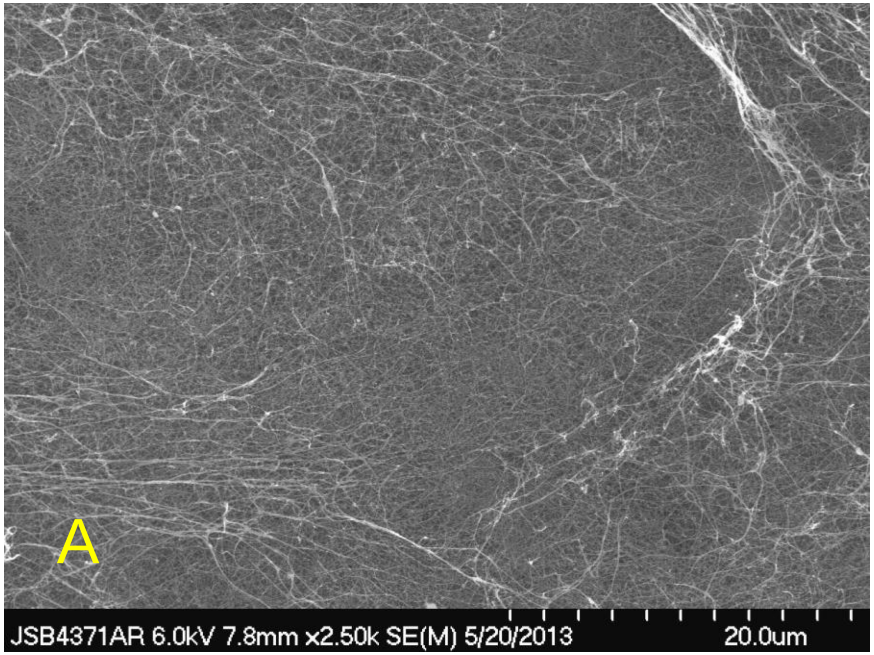
- Prof. Roberto Uribe (Kent State), NEO Beam electron beam facility

- Fellowship Funding- NASA Postdoctoral Program administrated by Oak Ridge Associated Universities

- Project Funding- NASA Space Technology Game Changing Development Program

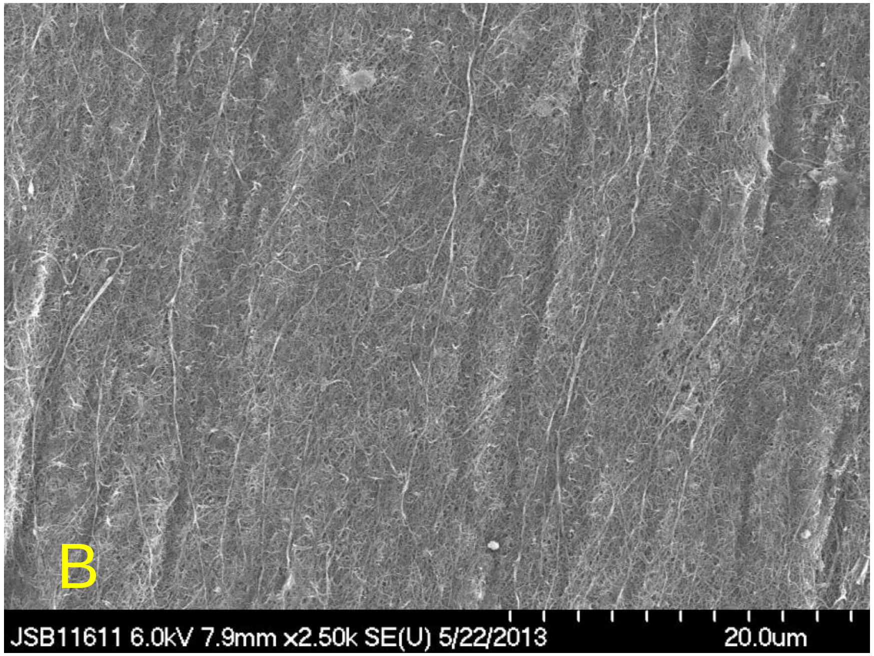
SEM Micrographs of Nanotube Sheet

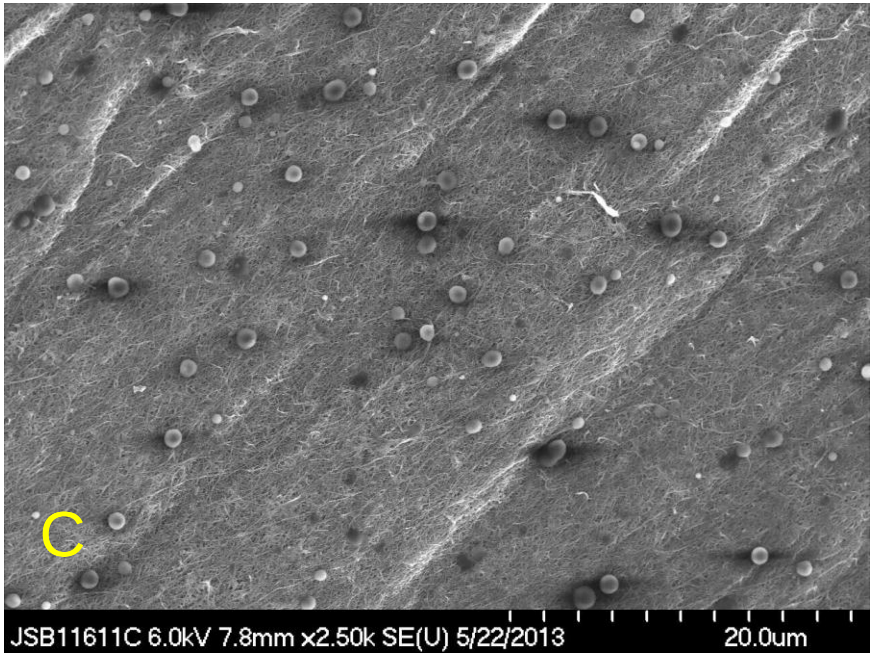


A. As Received

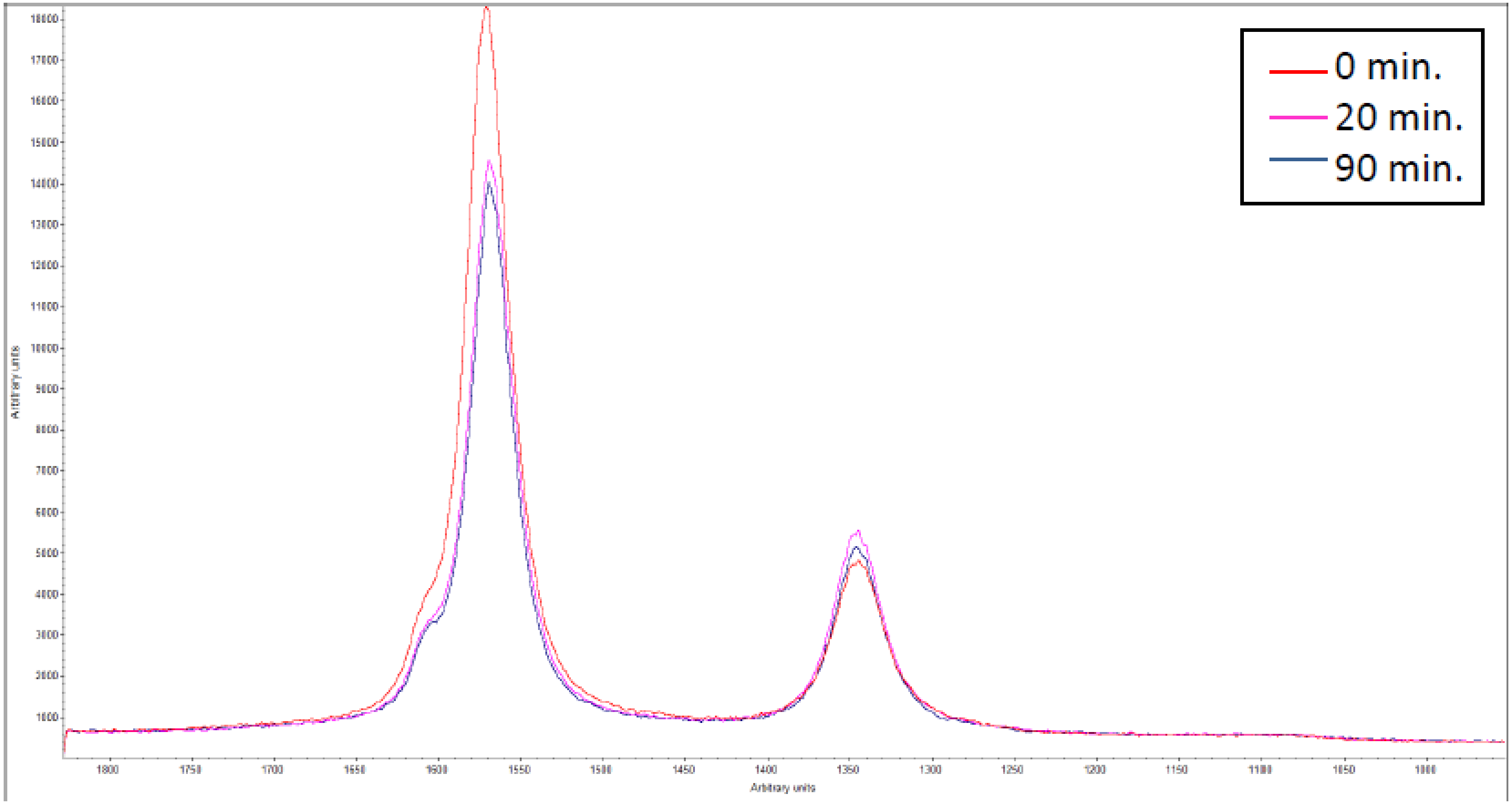
B. 14% Prestrain, 5 mol% OH

C. 14% Prestrain, 5 mol% OH, 90 min E Beam



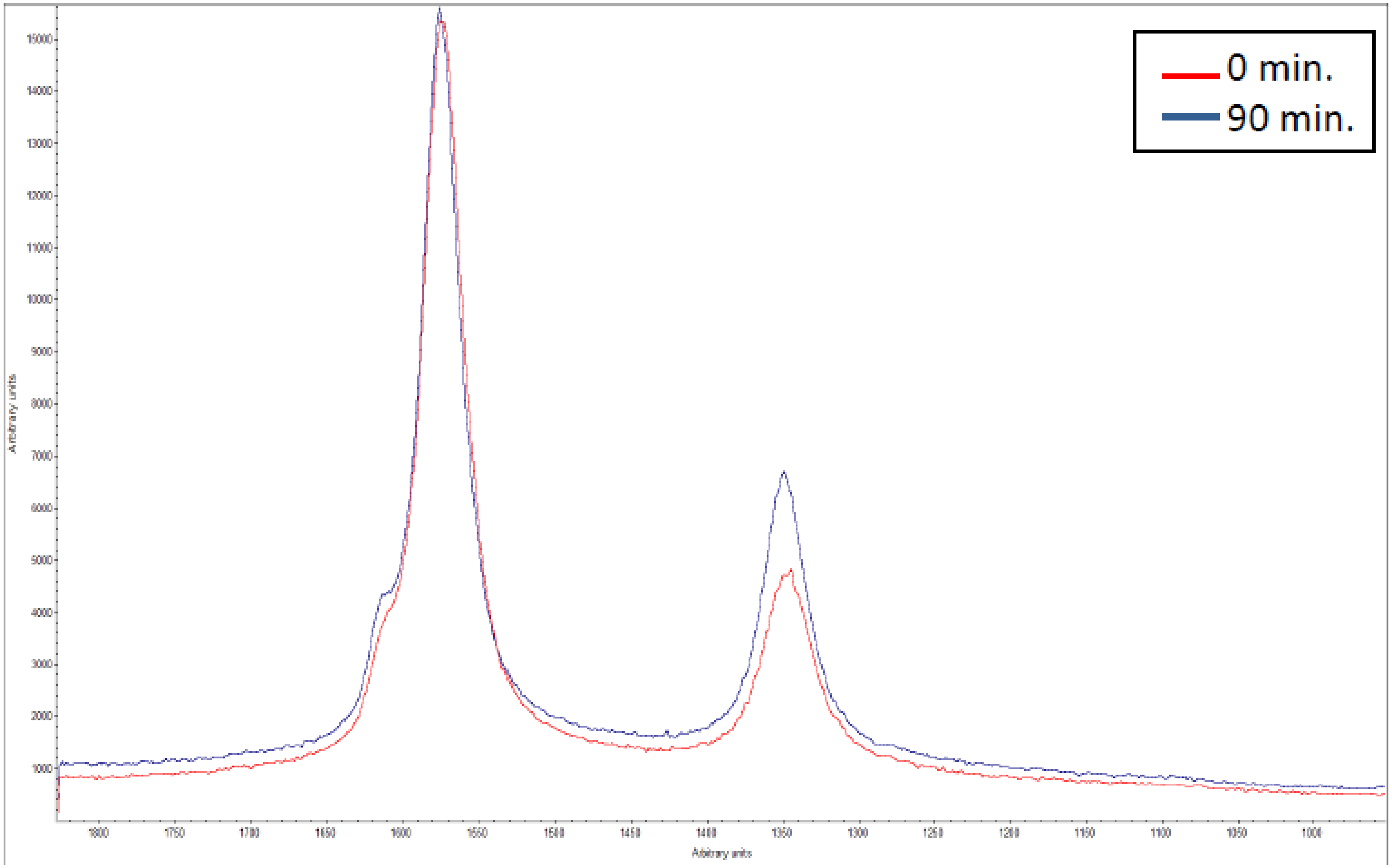


AR #5333



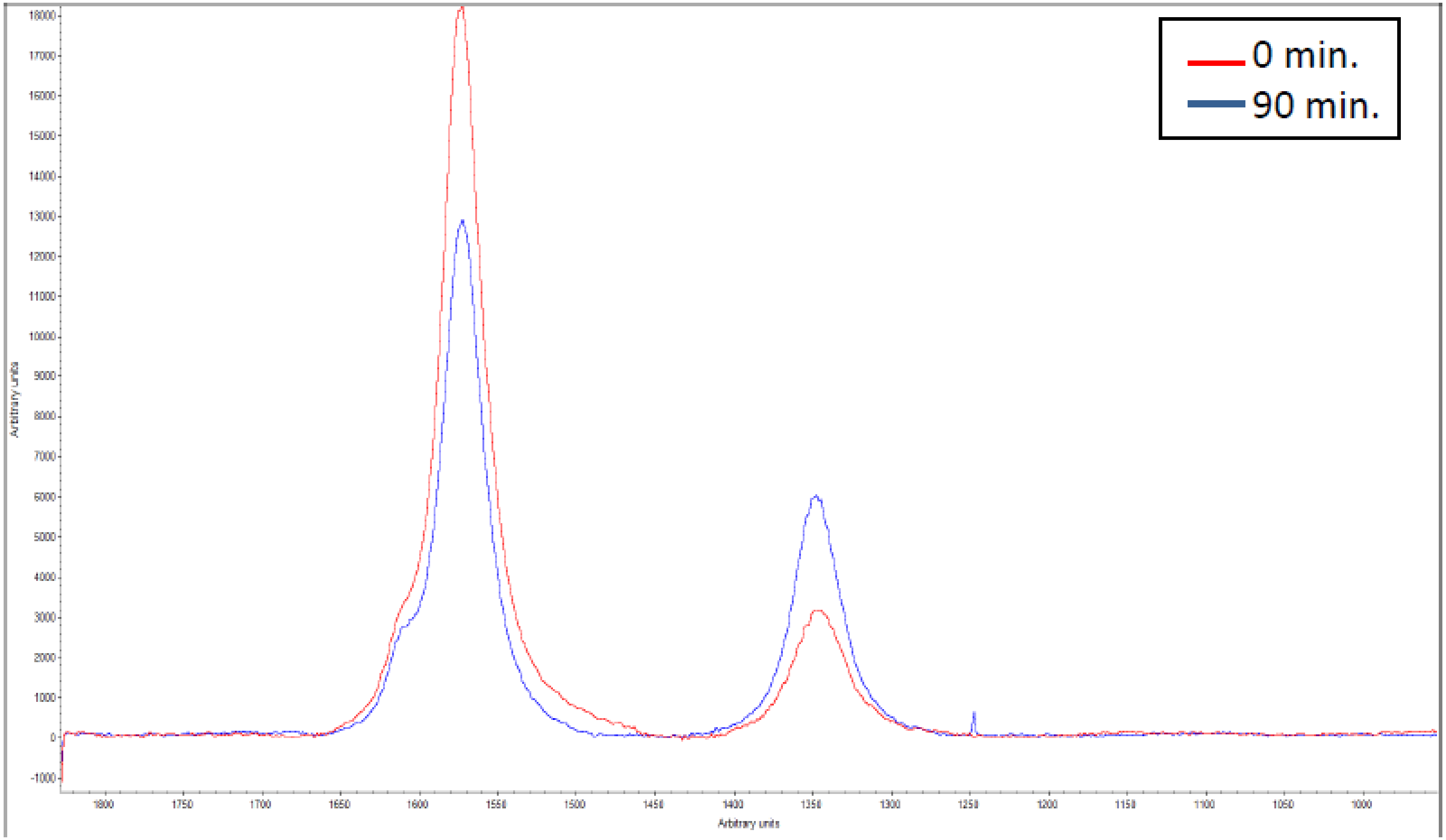
AR 5333	Time (min)		Disorder band					
		G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	18286.1	4830.6	1570.8	0.264	674830.0	137498.6	0.204
	20	14534.4	5479.4	1569.7	0.377	528274.4	171094.2	0.323
	90	13998.4	5140.9	1569.2	0.367	488926.5	145357.8	0.297

EtOH functionalized (#5333)



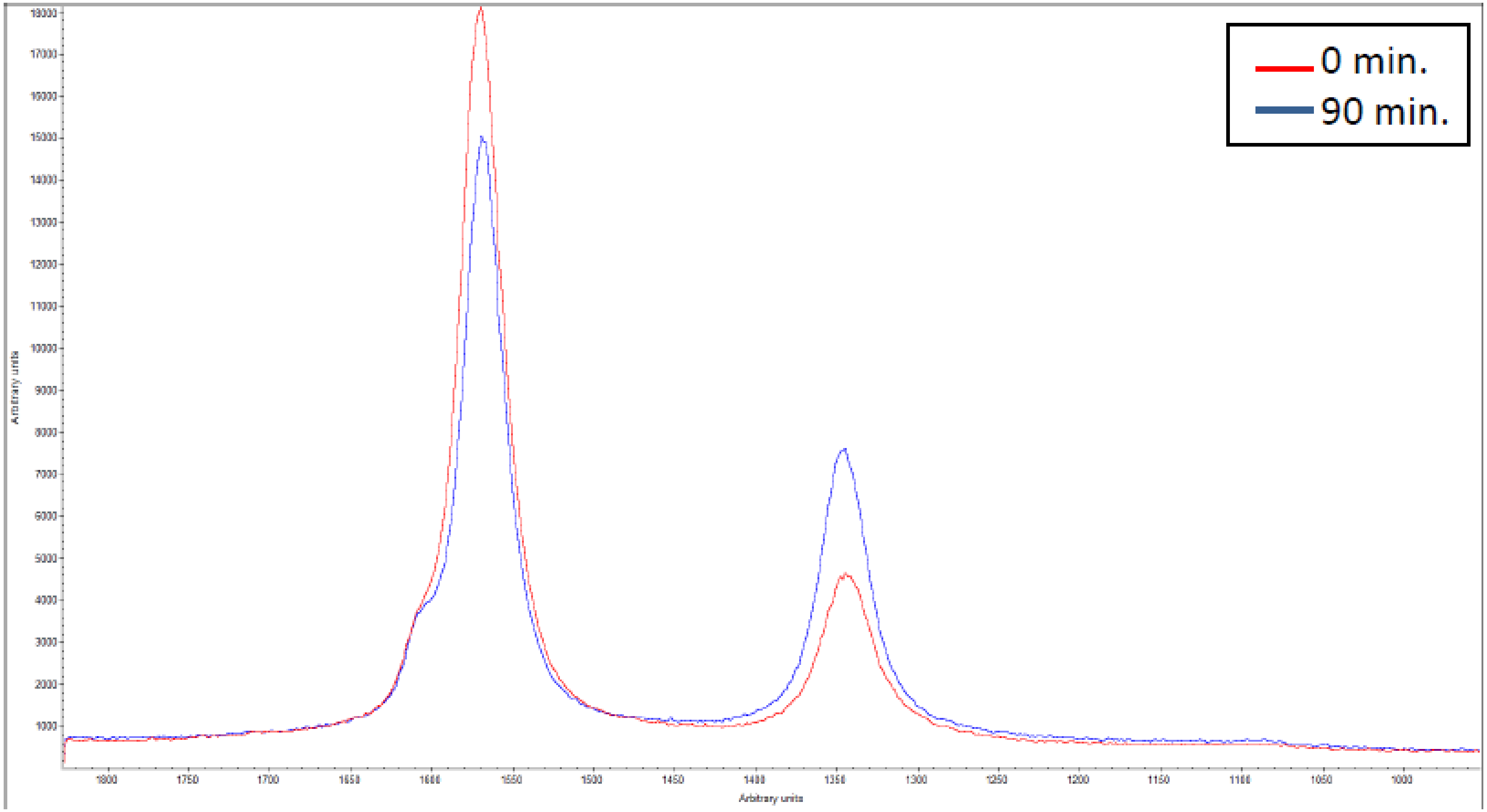
EtOH JSB 11391	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	15330.3	4718.8	1573.8	0.308	598052.7	141972.4	0.237
	90	15606.3	6699.2	1575.8	0.429	557340.1	189818.6	0.341

PrNH2 Functionalized (#5333)



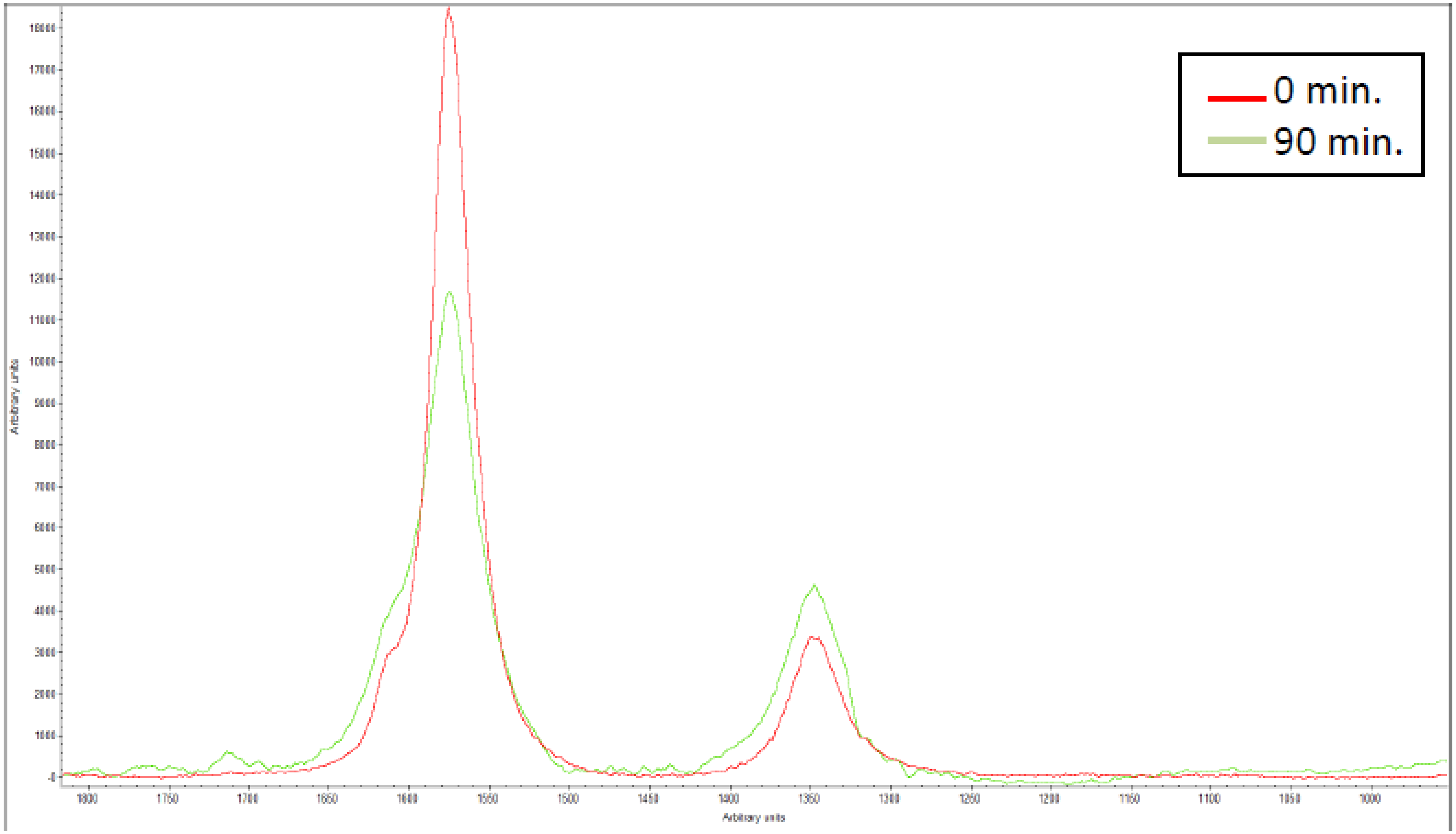
PrNH2 JSB11471	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A (G-band)	A (D-band)	A_D/A_G
	0	20435.0	5324.6	1572.3	0.261	735678.1	117483.5	0.160
	90	14246.4	7280.9	1572.3	0.511	523149.3	222635.6	0.426

Unfunctionalized 15% Prestrain (#5333)



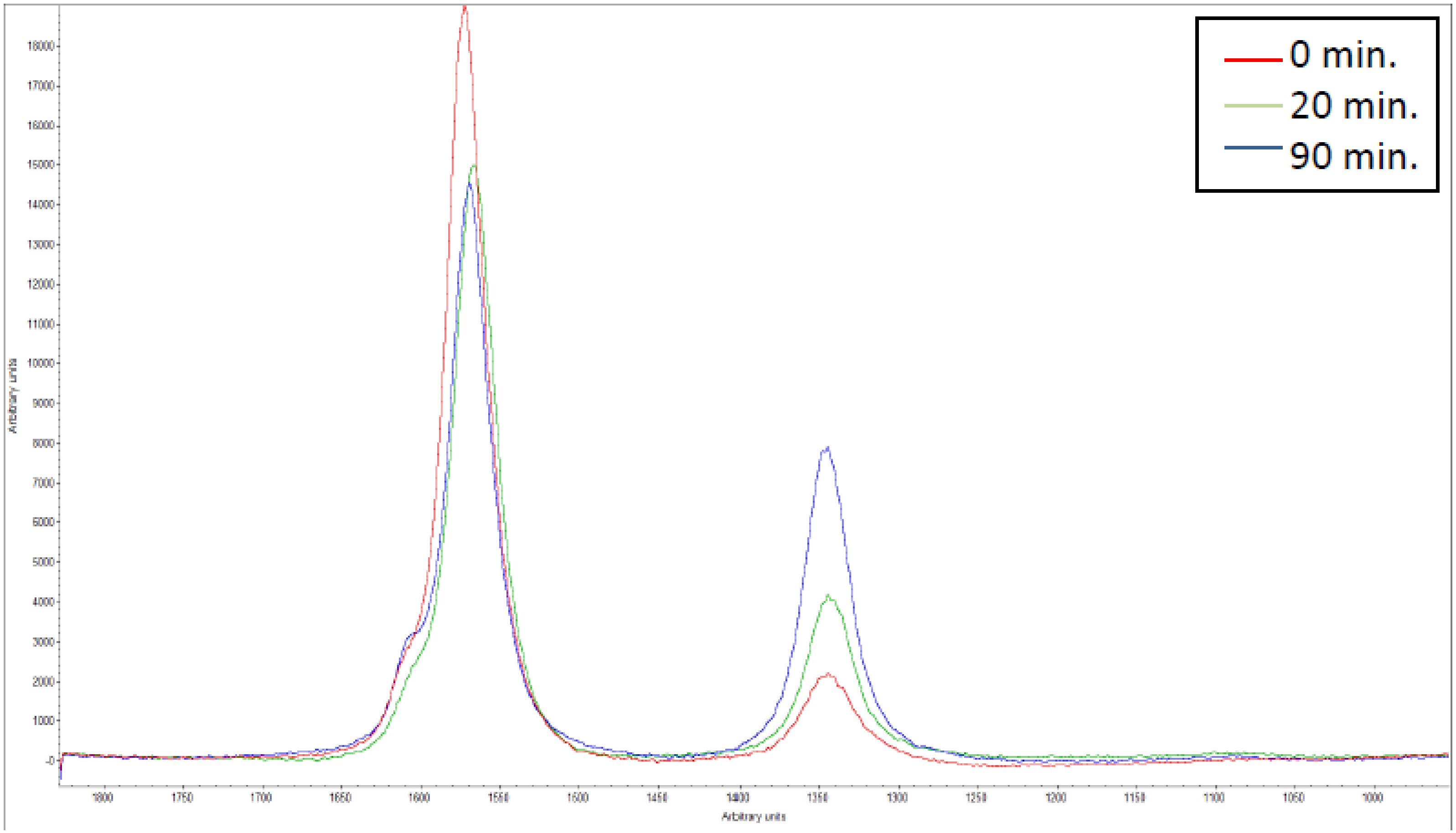
15% Prestrain JSB11652	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	18113.4	4642.4	1569.8	0.256	667741.2	132089.3	0.198
	90	15015.8	7636.5	1569.3	0.509	532588.3	231963.9	0.436

EtOH 13.5% Prestrain (#5333)



EtOH 13.5% Prestrain JSB11611	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	19842.3	4546.0	1575.3	0.230	665729.8	116935.8	0.176
	90	12306.5	3960.5	1576.4	0.322	492436.8	159288.9	0.323

AR 4371 (CNT sheets for panel fab)



AR 4371	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	19993.2	2979.7	1573.9	0.149	736802.9	84292.9	0.114
	20	16064.6	4804.8	1566.4	0.299	614848.9	147794.5	0.240
	90	18539.3	6846.4	1569.5	0.369	685277.1	196265.6	0.286